Short communication

# Lithium ion conduction in PVC–LiBF$_4$ electrolytes gelled with PMMA

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## Abstract

Hybrid, solid polymer electrolyte films consisting of poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), LiBF$_4$, and dibutyl phthalate (DBP) are described. FTIR studies and electrical conductivity measurements are carried out. The temperature dependence of ionic conductivity of the polymer films is explained on the basis of a free volume model. Conductivity studies of PVC–PMMA–LiBF$_4$–DBP complexes have been investigated at different salt concentrations. The highest ionic conductivity value ($2.482 \times 10^{-5}$ S cm$^{-1}$) is obtained for 8 mole ratio of LiBF$_4$ in the polymer complex at 304 K. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Polymer electrolyte; PVC/PMMA blend; LiBF$_4$; Plasticizer; FTIR; Impedance studies

## 1. Introduction

In recent years, ion conducting polymers have been extensively investigated because their application as an electrolyte in solid-state batteries. Since the conductivity of poly(ethylene oxide) (PEO)–salt complex was reported by Wright [1] in 1975, the polymer-based solid electrolytes have been of growing importance for rechargeable batteries with high specific energies [2–6]. Solid polymer electrolytes have many advantages such as no leakage, volumetric stability, solvent-free condition, easy handling, and wide electrochemical stability windows. A disadvantage of linear PEO-based electrolytes is their partially crystalline nature which results in low ionic conductivity at room temperature, and in time-dependent ionic conductivity due to the slow kinetics of crystallization of the polymer, because the conduction phases in the polymer electrolytes are amorphous phases containing electrolyte salts.

In the last few years, many approaches have been adopted to reduce the crystallinity of PEO-based electrolytes and increase the segmental mobility of the host polymer through co-polymerization, grafting, network formation, modification of macromolecules by pendant PEO systems [7] and plasticization of matrix polymers.

Poly(vinyl chloride) (PVC) can act as a mechanical stiffener in the electrolyte due to the immiscibility of PVC with the plasticizer. PVC-based polymer electrolyte systems, plasticized with ethylene carbonate and propylene carbonate, have been reported to be applicable to lithium and lithium-ion secondary batteries [8]. Poly(methyl methacrylate) (PMMA), as a host polymer, was first reported by Iijima et al. [9], and more recently by Bohnke et al. [10]. Appetecchi [11] studied the kinetics and stability of the lithium electrode in PMMA-based gel electrolytes. Rhoo et al. [12] reported the ionic conductivity of plasticized PVC/PMMA blended polymer electrolytes.

In this work, hybrid solid electrolyte films which consist of PVC, PMMA, LiBF$_4$, and dibutyl phthalate (DBP) are examined to overcome the problems inherent to gel electrolytes. The conductivity values of hybrid polymer complexes for different salt concentrations and temperatures are investigated and reported.

## 2. Experimental

The electrolytes were prepared from PVC (Aldrich, average molecular weight $1.5 \times 10^5$) and PMMA (Aldrich, average molecular weight $1.7 \times 10^5$), which were dried at 100°C under vacuum for 10 h. LiBF$_4$ (Aldrich) was dried at 70°C under vacuum for 24 h and DBP (Aldrich) was used without further purification. Appropriate quantities of

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Table 1
Conductivity values of PVC–PMMA–LiBF$_4$–DBP polymer complexes

| Sample | Polymer complex | $\sigma$ values ($\times 10^{-5}$ S cm$^{-1}$) | | | | | |
|--------|-----------------|--------|--------|--------|--------|--------|--------|
| | | 304 K | 328 K | 338 K | 348 K | 358 K | 373 K |
| F1 | 7.5–17.5–4–71 | 0.273 | 0.598 | 1.161 | 1.682 | 2.235 | 2.478 |
| F2 | 7.5–17.5–6–69 | 1.561 | 2.231 | 3.712 | 4.762 | 6.683 | 8.931 |
| F3 | 7.5–17.5–8–67 | 2.482 | 3.173 | 5.192 | 9.332 | 12.812 | 18.632 |
| F4 | 7.5–17.5–10–65 | 1.990 | 2.831 | 4.330 | 9.124 | 9.372 | 12.133 |

PVC, PMMA, and LiBF$_4$ (Table 1) were dissolved by addition, in sequence, to tetrahydrofuran (THF). After incorporating the required amount of the plasticizer (DBP), the solution was stirred for about 24 h before the electrolyte films were cast on finely-polished Teflon supports. The films were dried in a vacuum oven at 328 K at a pressure of $10^{-3}$ Torr for 24 h. FTIR studies were performed with a Perkin Elmer Paragon Model 500 spectrometer in the 4000–400 cm$^{-1}$ region. Conductivity measurements were carried out using a Keithley 3330 LCZ meter in the frequency range 40–100 kHz.
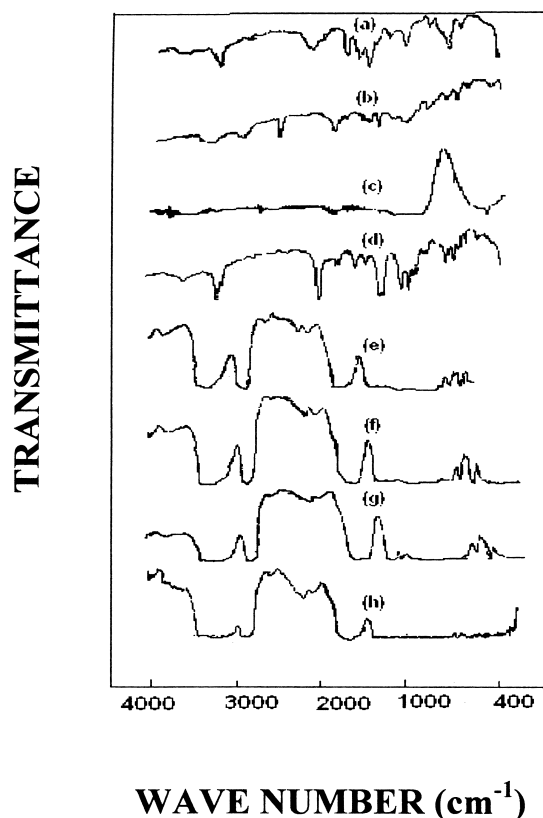


**WAVE NUMBER (cm$^{-1}$)**

Fig. 1. FTIR plots for (a) PVC; (b) PMMA; (c) LiBF$_4$; (d) DBP; (e) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–4–71 mol%); (f) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–6–69 mol%); (g) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–8–67 mol%); (h) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–10–65 mol%).

## 3. Results and discussion

### 3.1. FTIR spectroscopic studies

FTIR spectra were recorded in the transmittance mode. The FTIR spectra of PVC, PMMA, LiBF$_4$, DBP, and polymer complexes are shown in Fig. 1. The absorption peaks of PVC (1734, 1654, 1436, 1259 cm$^{-1}$), PMMA (2927, 1734, 1559, 1654, 1458, 1149, 840, 750 cm$^{-1}$), and DBP (2961, 1728, 1578, 1465, 1120, 748 cm$^{-1}$) are shifted in the polymer complexes. The vibrational bands of PVC (2360, 1339, 961, 669 cm$^{-1}$) are absent in the polymer complexes. The peaks at 1654, 1339, 1259, 961 and 600 cm$^{-1}$ are assigned to C=C stretching, CH$_2$ deformation, CH-rocking, *trans* CH wagging, and *cis* CH wagging vibrations, respectively, in PVC. The peaks at 2927 and 1734 cm$^{-1}$ are assigned to C−H stretching and C=O stretching vibrations, respectively, in PMMA. The peak at 1578 cm$^{-1}$ is assigned to C=C stretching vibration in DBP. The peaks at 2986, 1744, 1648, 1439, 1195 and 844 cm$^{-1}$ are assigned to C−H stretching, C=O stretching, C=C stretching, CH$_3$ stretching, −O−CH$_3$ stretching, and C−Cl stretching vibrations, respectively, in the polymer complexes [13]. The above analysis established the formation of polymer–salt complexes.

### 3.2. Conductivity studies

The impedance diagram for the PVC–PMMA–LiBF$_4$–DBP film (F3, Table 1; Fig. 2) at 304 K. The conductivity of this system is $2.482 \times 10^{-5}$ S cm$^{-1}$ at 304 K. This
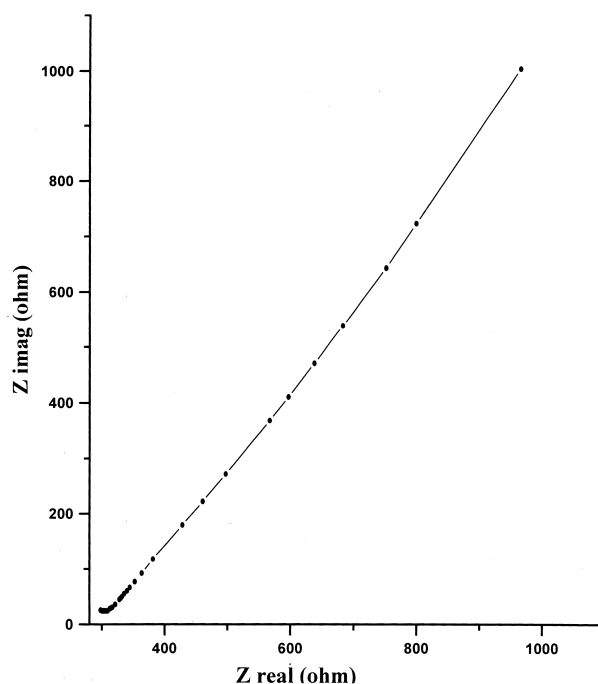


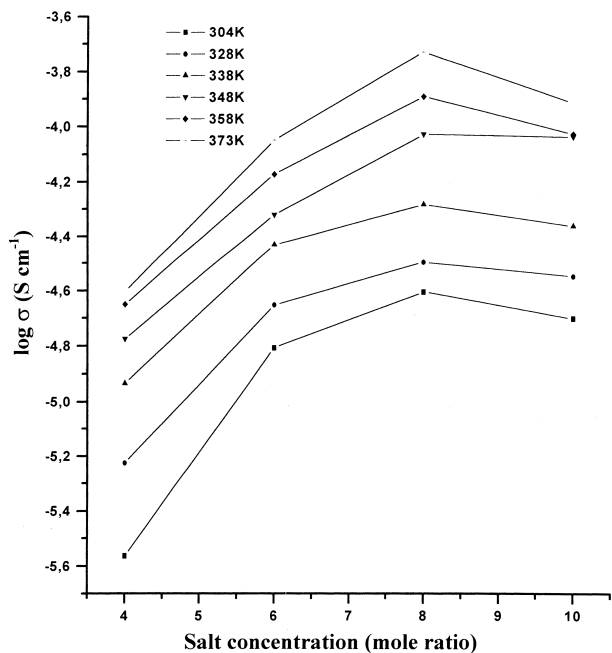Fig. 2. Impedance diagram for PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–8–67 mol%) at 304 K.

Fig. 3. Dependence of ionic conductivity on salt concentration for PVC–PMMA–LiBF$_4$–DBP polymer complex at different temperatures.

be rationalized by recognizing the free-volume model [14]. As the temperature increases, the polymer can expand easily and produce free volume. Thus, ions, solvated molecules, or polymer segments can move into the free volume [15]. The resulting conductivity represented by the overall mobility of ion and polymer is determined by the free volume around the polymer chains. Therefore, as the temperature increases, the free volume increases. This leads to an increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds.

The dependence of salt concentration on the ionic conductivity, $\sigma$, is described by examining plots of log $\sigma$ vs. LiBF$_4$ mole ratio for all samples, see Fig. 3. As a general trend, at low salt concentration, there is a build-up of charge carriers which results in an increase in ionic conductivity. The highest ionic conductivity for the polymer film (F3, Table 1) is found at salt concentration of 8 mole ratio over all the range of temperatures investigated. At high salt concentrations, build-up of charge carriers is offset by the retarding effect of ion clouds, thus, the ionic conductivity decreases as this latter effect begins to dominate. The conductivity decreases when the mole ratio of LiBF$_4$ is 10%. This may be due to restricted mobility of charge carriers in the more rigid matrix.

The Arrhenius plot of the ionic conductivity with a fixed amount of PVC/PMMA blend and various concentrations of salt with plasticizer is given in Fig. 4. The temperature dependence on the ionic conductivity is not
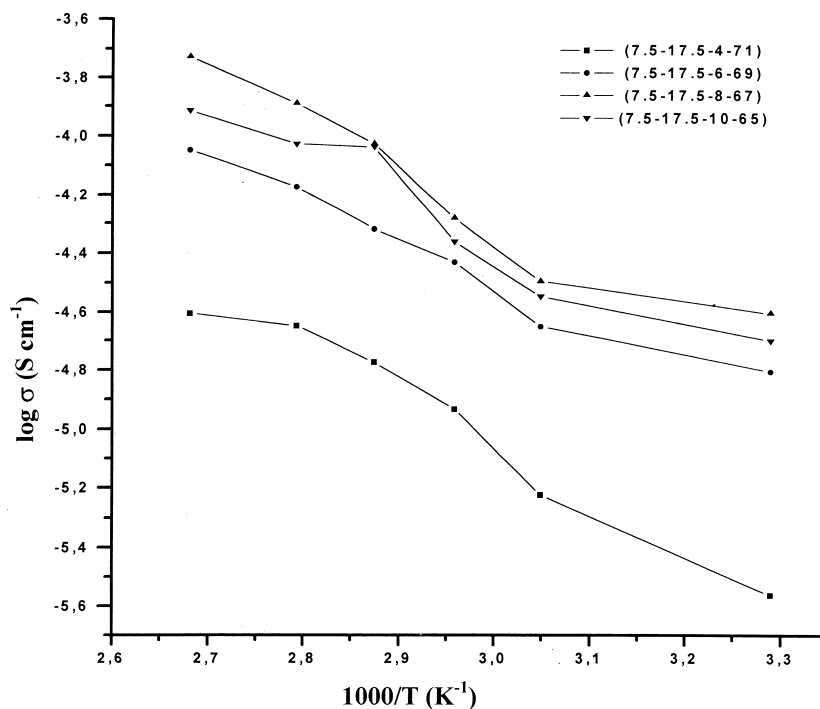
conductivity is similar to that of a PMMA-based gel electrolyte [11], but the film has better dimensional stability. The data given in Table 1 show that the conductivity increases with increase in temperature. This behaviour can



Fig. 4. Arrhenius plot of log conductivity against reciprocal temperature for PVC–PMMA–LiBF$_4$–DBP polymer complexes (a) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–4–71 mol%); (b) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–6–69 mol%); (c) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–8–67 mol%); (d) PVC–PMMA–LiBF$_4$–DBP (7.5–17.5–10–65 mol%).

linear, which suggests that ion conduction follows the Williams–Landel–Ferry (WLF) mechanism [16]. That is, ion transport in polymer electrolytes is correlated with polymer segmented motion [17].

## 4. Conclusions

Complex formation in PVC–PMMA–LiBF$_4$ has been confirmed from FTIR studies. The highest ionic conductivity is shown at a salt concentration of 8 mole ratio in the overall range of temperatures studied. The temperature dependence of ionic conductivity is explained on the basis of the free volume model.

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